STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

(11) 2 July 1976

(12)

(9) Progress Report No. 1, 15 May - 14 June 76

May 15 - June 14, 1976

(6) DESENSITIZATION OF EXPLOSIVE MATERIALS.

(10) By: Howard M. Peters and John M. Guimont

(12) 6 p.

Prepared for:

Scientific Officer, Director Vehicle Technology Program
Assistant Chief for Technology
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

Attention: LT Richard S. Miller, Code 211

(15) Contract Number N00014-76-C-0810

(16) SRI Project PYU-5374

Approved:

M. E. Hill, Director
Chemistry Laboratory

Introduction and Summary

The objective of the work reported here is to determine the generality of the recent discovery that substitution of fluorine for hydrogen in an explosive material leads to desensitization. In earlier work for Lawrence Livermore Laboratory (ERDA) it was discovered that substitution of the $-CH_2-$ group in FEFO with a $-CF_2-$ group reduces the sensitivity to impact and low velocity detonation (LVD). In addition

$$FC(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2F \quad \text{(FEFO)}$$

$$\downarrow \text{ Reduced sensitivity}$$

$$FC(NO_2)_2CH_2OCF_2OCH_2C(NO_2)_2F \quad \text{(DFF)}$$

to achieving reduced sensitivity, the physical properties of DFF are more desirable than FEFO. A comparison of the sensitivity characteristics and physical properties of FEFO and DFF are shown in Table 1.

In order to generalize our hypothesis that the substitution of fluorine for hydrogen will desensitize an explosive, we will first prepare formals analogous to FEFO and DFF and determine their sensitivity characteristics.

During the first report period the sensitivity testing equipment was calibrated materials were ordered, and laboratory work begun.

Synthesis

Table 2 shows the formals and difluoroformals which we propose to study. We have begun the synthesis of TEFO and its difluoro analog. TEFO has already been reported,[1] and a sample has been prepared for testing. Although some of the sensitivity characteristics of TEFO are already known, they will be repeated so that there will be a direct comparison of the test results using the same equipment. Difluoro-TEFO

1. M. E. Hill and K. G. Shipp, U.S. Patent 3,526,667, (1970).

Table 1

PHYSICAL PROPERTIES OF FEFO AND DFF

	$[FC(NO_2)_2CH_2O]_2CH_2$ FEFO	$[FC(NO_2)_2CH_2O]_2CF_2$ DFF
Mol wt	320.1	356.1
bp, °C (mm)	110 (0.3)	70 (0.003)
mp, °C	+14	-17
vp, μ (25°C)	0.16	1.6
ρ, g/cc (°C)	1.59	1.67 (27)
ΔH_f^o, kcal/mol	-178	-275
DTA, °C	exotherm starts 209	exotherm starts 228 max 250
CRT, cc	0.04-0.1	0.04-0.06
LVD	1500-1800	225-325
HVD	80-85	77
Impact, kg-cm	6	135

Notes: CRT (chemical reactivity test) = Volume of gas in a cubic centimeter released at 100°C for 8 hr.

Impact (kg-cm) = Product of a 3-kilogram weight falling one centimeter.

LVD (low velocity detonation) = Number of 1-mm cards necessary to reduce detonating explosive impact.

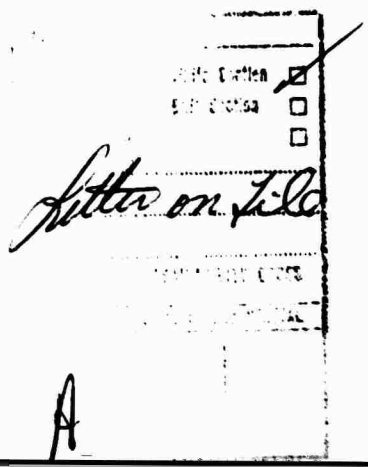

Table 2

LINEAR FORMALS AND DIFLUOROFORMALS

$(RO)_2CH_2$ (Formals)		$(RO)_2CF_2$ (Fluoroformals)	
Compound	Structure	Compound	Structure
FEFO	$[FC(NO_2)_2CH_2O]_2\overset{*}{C}H_2$	DFF	$[FC(NO_2)_2CH_2O]_2\overset{*}{C}F_2$
DNPF	$[H_3CC(NO_2)_2CH_2O]_2\overset{*}{C}H_2$	NPFF	$[H_3CC(NO_2)_2CH_2O]_2\overset{*}{C}F_2$
TDPF	$[CF_3OCH_2C(NO_2)_2CH_2O]_2\overset{*}{C}H_2$	OTT	$[CF_3OCH_2C(NO_2)_2CH_2O]_2\overset{*}{C}F_2$
TEFO	$[C(NO_2)_3CH_2O]_2\overset{*}{C}H_2$	‡	$[C(NO_2)_3CH_2O]_2\overset{*}{C}F_2$
‡	$FC(NO_2)_2CH_2O\overset{*}{C}H_2OCH_2C(NO_2)F_2$	MFF	$FC(NO_2)_2CH_2O\overset{*}{C}F_2OCH_2C(NO_2)F_2$
‡	$FC(NO_2)_2CH_2O\overset{*}{C}H_2OCH_2CF_3$	TMFF	$FC(NO_2)_2CH_2O\overset{*}{C}F_2OCH_2CF_3$
‡	$[FC(NO_2)_2CH_2O\overset{*}{C}H_2OCH_2]_2C(NO_2)_2$	ADDF	$[FC(NO_2)_2CH_2O\overset{*}{C}F_2OCH_2]_2C(NO_2)_2$
‡	$FC(NO_2)_2CH_2O\overset{*}{C}H_2\overset{*}{C}H_2OCH_2C(NO_2)_2F$	HTD	$FC(NO_2)_2CH_2O\overset{*}{C}F_2\overset{*}{C}F_2OCH_2C(NO_2)_2F$

* Site of change.

‡ Not previously reported.

is not a known compound, but its synthesis using known procedures[2,3] (Eqs 1-2) should not be difficult. A sample of the carbonate has been

$$2C(NO_2)_3CH_2OH + COCl_2 \xrightarrow[(1)]{} [C(NO_2)_3CH_2O]_2C{=}O$$

$$[C(NO_2)_3CH_2O]_2C{=}O + SF_4 \xrightarrow[(2)]{HF} [C(NO_2)_3CH_2O]_2CF_2$$

prepared, and the fluorination reaction is planned during the next report period.

The second formal pair which we plan to prepare and characterize, is ADDF and its $-CH_2-$ analog. ADDF has been reported,[4] and a literature survey indicates that there are two possible routes to the $-CH_2-$ analog as shown in Eqs 3-4 and Eqs 5-6.

$$FC(NO_2)_2CH_2OH + HCl + HCHO \xrightarrow[(3)]{} FC(NO_2)_2CH_2OCH_2Cl$$

$$2FC(NO_2)_2CH_2OCH_2Cl + \text{A-DIOL} \xrightarrow[(4)]{} [FC(NO_2)_2CH_2OCH_2OCH_2]_2C(NO_2)_2$$

$$\text{DINOL} + (CH_2O)_3 + AlCl_3 \xrightarrow[(5)]{} (ClCH_2OCH_2)_2C(NO_2)_2$$

$$(ClCH_2OCH_2)_2C(NO_2)_2 + 2FC(NO_2)_2CH_2OH \xrightarrow[(6)]{} [FC(NO_2)_2CH_2OCH_2OCH_2]_2C(NO_2)_2$$

---

2. T. N. Hall, J. Org. Chem. 33, 4457 (1968).
3. P. E. Aldrich and W. A. Sheppard, J. Org. Chem. 29, 11 (1964).
4. SRI Report, May 1, 1971 to January 31, 1973, Contract No. AT(04-3)-115.

The fluorodinitroethyl, chloromethyl ether Eq 3, and 1,3-bischloromethyl 2,2-dinitropropyl ether, Eq 5, have been reported;[5] [6] the condensation of chloromethyl ethers with acidic alcohols is well known.

Future Work

During the next report period we plan to fluorinate bistrinitroethyl carbonate to give difluoro-TEFO and begin the sensitivity tests on TEFO and difluoro-TEFO. We will also begin the synthetic effort to prepare ADDF and its $-CH_2-$ analog.

---

5. ALWT-High Energy Plasticizer and Binder Synthesis, Final Report, 15 February 1976, G. W. Lawrence, et al.
6. H. G. Adolf and M. J. Kamlet, J. Org. Chem. 34, 45, (1969).

DISTRIBUTION LIST

Address	DODAAD Code	No. Copies
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217		
Scientific Officer	N00014	1
Administrative Contracting Officer	S0507A	1
Director, Naval Research Laboratory Attn: Code 2627 Washington, D.C. 20375	N00173	6
Office of Naval Research Department of the Navy Arlington, Virginia 22217 Attn: Code 1021P	N00014	6
Defense Documentation Center Bldg. 5, Cameron Station Alexandria, Virginia 22314	S47031	12
Office of Naval Research Room 447 760 Market Street San Francisco, Ca. 94102 Attn: Phillip Miller	N62887	1